Equilibrium dec12

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Ionic Eq^m

- H_2O
- pH Calculation
  - → S.A, S.B sol^n & their mix
  - → W.A, W.B & their mix
  - → Ostwald's Dilution Law
  - → W.A + S.A & W.B + S.B
  - → Diprotic & Triprotic weak Acid sol^n
  - → Complete Neutralization Case → Salt Hydrolysis
  - → Incomplete Neutralization → Buffer Solution
- Titration Curves
- Solubility & Solubility product

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① S.A & S.B & their mixtures

25°C

$H_2O \rightleftharpoons H^+ + \bar{O}H$ → H_2O alone

$\boxed{\alpha = 1.8\times10^{-9}}$

$[H^+]_{water} = 10^{-7}M$

HCl → $H_2O \rightleftharpoons H^+ + OH^-$, $H^+ + Cl^-$ → Common ion

$\alpha_1 \Rightarrow$ New degree of ionization at new eq^m which is less than 1.8×10^{-9}

$\boxed{[H^+]_w < 10^{-7}M}$

$K_w \Rightarrow$ Same equal to 10^{-14}

→ for numericals $[H^+]_w \approx 10^{-7}M$

Common ion Effect (CIE)
↳ effect in which degree of ionization of Weak Electrolyte decreases due to increase in Conc of Common ion.
Eq^m of W.E shifts BACKWARD.

# H_2O (W.E) ⇒ α_1 ⇒ when HCl (0.1M) is added in H_2O
⇓ α_2 ⇒ when HCl (0.2M) is added in H_2O

i) ✓ $\alpha_1 > \alpha_2$
ii) $\alpha_1 = \alpha_2$
(iii) $\alpha_1 < \alpha_2$
(iv) Both (i) & (iii) can be present

for such cases

$[H^+]_{Total} = [H^+]_w + [H^+]_{Acid}$

a) if $[H^+]_{Acid} \geq 10^{-6}M$
$[H^+]_{water}$ can be neglected
$[H^+]_{Total} \approx [H^+]_{Acid}$
$\boxed{pH = -\log[H^+]_{Acid}}$

b) if $[H^+]_{Acid} < 10^{-6}M$
$\boxed{[H^+]_{Total} = [H^+]_{Water} + [H^+]_{Acid}}$
$pH = -\log[H^+]_{Total}$

Similarly SB → H_2O

a) $[\bar{O}H]_{Base} \geq 10^{-6}M$
$[OH^-]_{Total} \approx [OH^-]_{SB}$

b) $[OH^-]_{Base} < 10^{-6}M$
$[OH^-]_{Total} = [OH^-]_w + [OH^-]_{SB}$
$= 10^{-7} + [OH^-]_{SB}$

Q. pH of sol^n?

① 0.1M HCl(aq) (10^{-1})
$[H^+] = [HCl] = 10^{-1}M$
$pH = -\log 10^{-1} = 1$

② $10^{-4}M$ $H_2SO_4(aq)$
$[H^+] = N_{H_2SO_4} = 2\times10^{-4}$
$[H^+] = 2\times10^{-4}M$
$pH = -\log(2\times10^{-4}) = 4 - \log 2$
$= 4 - 0.3$
$= 3.7$

$-\log(a\times10^{-b}) = b - \log a$
$-\log(2\times10^{-5}) = 5 - \log 2$
$= 5 - 0.3$
$= \boxed{4.7}$

# $-\log(a\times b\times10^{-c}) = c - \log a - \log b$

③ $10^{-7}M$ HCl(aq)
$[H^+]_{HCl} < 10^{-6}M$
$[H^+]_{Total} = 10^{-7} + [H^+]_{HCl}$
$= 10^{-7} + 10^{-7}$
$= 2\times10^{-7}$
$pH = 7 - \log 2$
$= 7 - 0.3$
$= \boxed{6.7}$

④ $10^{-8}M$ $Ca(OH)_2(aq)$
$[OH^-] = (2\times10^{-8}M) < 10^{-6}M$
$[OH^-]_{Total} = [\bar{O}H]_w + [OH^-]_{Ca(OH)_2}$
$= 10^{-7} + (2\times10^{-8})$
$= 10^{-7}(1 + (2\times0.1))$
$= 1.2\times10^{-7} = 12\times10^{-8} = 4\times3\times10^{-8}$

$pOH = 8 - \log 4 - \log 3$
$= 8 - 0.6 - 0.47$
$= 6.93$
$pH = 14 - 6.93$
$= 7.07$

5) 100ml H_2O + 100ml, 0.1M NaOH(aq)
m moles of NaOH = $(100\times0.1) = 10$ m moles
$[NaOH]_{new} = \frac{10}{200} = \frac{1}{20}M = 0.05M = 5\times10^{-2}M$
$[OH^-] = 5\times10^{-2}M$
$pOH = 2 - \log 5 = 2 - 0.7$
$= 1.3$
$pH = 14 - 1.3$
$= \boxed{12.7}$ ✓

⑥ 500ml H_2O + 500ml, 0.1M $H_2SO_4(aq)$
$[H_2SO_4]_{new} = \frac{500\times0.1}{1000}$
$[H^+] = \cancel{2}\times\frac{\cancel{500}\times0.1}{\cancel{1000}} = 10^{-1}$ pH = 1

Note:-
pH = $-\log(N_{Acid})$
pH = $-\log[H^+]$
pH = $-\log(N_{H^+})$

$[OH^-] = N_{OH^-}$
$[H^+] = N_{H^+}$
$n_f(H^+) = 1$
$n_f(OH^-) = 1$

$\boxed{N_{Acid} = N_{H^+} = [H^+]}$
↳ irrespective of No. of H^+ in acid

$\boxed{n_f\times[H^+] = N_{H^+}}$

Q. Which is having highest pH?
1) 0.1M HCl (0.1N)
2) 0.1N H_2SO_4
3) 0.1N H_3PO_4 (strong Acid)
✓ 4) All have same pH

# pH of Mix of SA & S.B

ⓐ Mix of only S.As
$[H^+]_w \Rightarrow$ Ignored
$N_{H^+} = [H^+]_{Total} = \frac{N_1V_1 + N_2V_2 + N_3V_3 + ---}{\text{Total Volume}}$
$pH = -\log[H^+]_{Total}$

ⓑ only mix of S.Bs
$[\bar{O}H]_{water} \rightarrow$ ignored
N_{OH} or $[OH^-]_{Total} = \frac{N_1V_1 + N_2V_2 + ---}{\text{Total Vol.}}$
$pOH = -\log[OH^-]$
$pH = 14 - pOH$

ⓒ Mix of S.A + S.B
(i) $\boxed{\Sigma N_aV_a} > \Sigma N_bV_b$ → Total eq or meq of $\bar{O}H$
↳ Total equivalents or meq of H^+
Sol^n is Acidic
N_{H^+} or $[H^+]_{Resultant} = \frac{\Sigma N_aV_a - \Sigma N_bV_b}{\text{Total Volume}}$
$pH = -\log[H^+]$

~~pH~~ = 3
$[H^+] = 10^{-pH}$
$= 10^{-3}$

(ii) $\Sigma N_aV_a < \Sigma N_bV_b$
Sol^n is Basic
$[OH^-]_{Resultant} = \frac{\Sigma N_bV_b - \Sigma N_aV_a}{\text{Total Volume}}$
$pOH = -\log[\bar{O}H]$
$\boxed{pH = 14 - pOH}$

(iii) $\Sigma N_aV_a = \Sigma N_bV_b$
Sol^n is Neutral
$\boxed{pH = pOH = 7}$

Q. pH of Sol^n

i) 100ml, 0.1M HCl + 200ml, 0.1M NaOH (0.1N) + 300ml, 0.1M KOH (0.1N)
$\Sigma N_aV_a = 10$ meq
$\Sigma N_bV_b = (200\times0.1) + (300\times0.1) = 50$ meq
Sol^n is BASIC
$[OH^-]_{net} = \frac{50 - 10}{600} = \frac{40}{600} = \frac{2}{30} = \frac{1}{15}M$
$pOH = -\log\frac{1}{(5\times3)} = \log 5 + \log 3$
$= 0.7 + 0.47$
$\boxed{pH = 14 - pOH}$

(ii) 500ml, 0.1M H_2SO_4 (0.2N) + 500ml, 0.1M HCl + 500ml H_2O
$[H^+]_{net} = \frac{(0.2\times500) + (0.1\times500)}{1000 + 500} = \frac{150}{1500} = \frac{1}{10} = 0.1$ $\boxed{pH = 1}$

(iii) 100ml, 0.1M $Ca(OH)_2$ (0.2N) + 100ml, 0.1M NaOH
$[OH^-] = \frac{30}{200}M = \frac{3}{20}$
$pOH = -\log\left(\frac{3}{20}\right) = \log\left(\frac{20}{3}\right) = \log\left(\frac{2\times10}{3}\right)$
$= \log 2 + \log 10 - \log 3$
$= 0.3 + 1 - 0.47$
$= 1.3 - 0.47$
$\boxed{pH = 14 - pOH}$

(iv) equal vol. of sol^n of pH = 3, 4, 6 are mixed
$[H^+] = 10^{-3}M$, V ml; $[H^+] = 10^{-4}M$, V ml; $10^{-6}M = [H^+]$, V ml

$[H^+]_{Total} = \frac{(10^{-3}\times V) + (10^{-4}V) + (10^{-6}V)}{3V}$
$= \frac{10^{-3}}{3}[1 + 0.1 + 0.001]$
$= \frac{1.101\times10^{-3}}{3}$
$= \frac{11.01\times10^{-4}}{3} \approx \frac{11\times10^{-4}}{3}$

$pH = -\log\left(\frac{11\times10^{-4}}{3}\right)$
$= -\log(11\times10^{-4}) + \log 3$
$= 4 - \log 11 + \log 3$
$= 4 - 1.043 + 0.47$

(v) equal volume Sol^n of pH = 7, 9 are mixed
$[H^+] = \frac{10^{-7} + 10^{-9}}{2}$
$= \frac{10^{-7}(1 + 0.01)}{2}$
$pH = -\log 10^{-7} + \log 2$
$= 7 + 0.3$
$= \boxed{7.3}$ ✓

Ⅱ pH of Weak Acid, Weak Base AND OSTWALD'S DILUTION LAW

i) WA — Monobasic Weak Acid

eg. CH_3COOH → H_2O

$CH_3COOH(aq) \rightleftharpoons H^+_{(aq)} + CH_3COO^-_{(aq)}$

or

$CH_3COOH_{(aq)} + H_2O_{(l)} \rightleftharpoons CH_3COO^- + H_3O^+(aq)$

# $CH_3COOH(aq) \rightleftharpoons CH_3COO^-(aq) + H^+(aq)$

	$CH_3COOH(aq)$	$CH_3COO^-(aq)$	$H^+(aq)$
t=0	C mol/L	0	0
at eq^m	$C(1-\alpha)$ $C - C\alpha$	$C\alpha$	$\boxed{C\alpha}$

$K_{eq} = K_a = \frac{[CH_3COO^-][H^+]}{[CH_3COOH]} = \frac{(\cancel{C}\alpha)(C\alpha)}{\cancel{C}(1-\alpha)} = \frac{C\alpha^2}{(1-\alpha)}$

K_a → eq^m const of Acid or Ionization const of Acid

Strong Acid have Very High K_a value

$K_a = \frac{C\alpha^2}{(1-\alpha)}$

if % ionization ≤ 10%
$\alpha \leq 0.1$ or 10^{-1}
$\boxed{K_a \leq 10^{-2}}$
$\alpha^2 \leq 10^{-2}$
$1 - \alpha \approx 1$, $\alpha << 1$
- $\boxed{K_a = C\alpha^2}$
- $\alpha^2 = \frac{K_a}{C}$ ⇒ $\boxed{\alpha = \sqrt{\frac{K_a}{C}}}$
- $[H^+] = C\alpha = C\sqrt{\frac{K_a}{C}} = \sqrt{C\cdot K_a}$

$-\log[H^+] = -\log(C\cdot K_a)^{1/2}$
$= \frac{1}{2}[-\log C - \log K_a]$
$\boxed{pH = \frac{1}{2}[pK_a - \log C]}$

If % ionization > 10%
$\alpha > 10^{-1}$
$\alpha^2 > 10^{-2}$ ⇒ $\frac{K_a}{C} > 10^{-2}$
$1 - \alpha \neq 1$
- $K_a = \frac{C\alpha^2}{1-\alpha}$

Get α By Solving Quadratic Eq^n
$[H^+] = C\alpha$
$\boxed{pH = -\log[H^+]}$

Q. 0.1M $CH_3COOH(aq)$
$K_a = 1.8\times10^{-5}$
pH = ? α = ?

Sol^n: $\frac{K_a}{C} = \frac{1.8\times10^{-5}}{10^{-1}} = 1.8\times10^{-4} < 10^{-2}$
$(1 - \alpha \approx 1)$

$\alpha = \sqrt{\frac{K_a}{C}} = \sqrt{\frac{1.8\times10^{-5}}{10^{-1}}} = \sqrt{1.8\times10^{-2}}$

$pH = \frac{1}{2}[pK_a - \log C]$
$= \frac{1}{2}[(5 - \log 1.8) - \log 10^{-1}]$
$= \frac{1}{2}[5 - \log 6 - \log 3 + \log 10 + 1]$
$= \frac{1}{2}[5 - 0.77 - 0.47 + 1 + 1]$
$= \frac{1}{2}[7 - 0.77 - 0.47]$

Q. HA (0.1M) is weak Acid Having $K_a = 10^{-2}$
pH = ?

Sol^n:- $\frac{K_a}{C} = \frac{10^{-2}}{10^{-1}} = 10^{-1} > 10^{-2}$
$1 - \alpha \neq 1$
$K_a = \frac{C\alpha^2}{1-\alpha}$ ⇒ $10^{-2} = \frac{10^{-1}(\alpha^2)}{1-\alpha}$
$10^{-2} - 10^{-2}\alpha = 10^{-1}\alpha^2$
$\alpha^2 + 10^{-1}\alpha - 10^{-1} = 0$

$\alpha = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$
$= \frac{-(10^{-1}) \pm \sqrt{10^{-2} + 4\times10^{-1}}}{2}$

$\boxed{[H^+] = C\alpha}$
$\boxed{pH = -\log[H^+]}$

(ii) Weak Base (Single OH^-)

eg. $NH_4OH(aq) \rightleftharpoons \overset{+}{N}H_4(aq) + \overset{-}{O}H(aq)$
$NH_3(aq)$

	$NH_4OH(aq)$	$NH_4^+(aq)$	$OH^-(aq)$
	C mol/L	0	0
at eq^m	$C - C\alpha$	$C\alpha$	$C\alpha$

$K_b = \frac{[NH_4^+][OH^-]}{[NH_4OH]}$

$\boxed{K_b = \frac{C\alpha^2}{1-\alpha}}$

→ if ionization ≤ 10%
$1 - \alpha \approx 1$ $\boxed{K_b = C\alpha^2}$ $\boxed{\alpha = \sqrt{\frac{K_b}{C}}}$ $\boxed{[OH^-] = C\alpha = \sqrt{C\cdot K_b}}$ $\boxed{pOH = \frac{1}{2}[pK_b - \log C]}$ $\boxed{pH = 14 - pOH}$

→ if ionization > 10%
$1 - \alpha \neq 1$
$K_b = \frac{C\alpha^2}{1-\alpha}$
α = ✓
$[OH^-] = C\alpha$
$pOH = -\log[OH^-]$
$\boxed{pH = 14 - pOH}$

# Ostwald's Dilution Law
↳ only for sol^n of Weak Electrolyte

" On Dilution (Add^n of H_2O) of sol^n of weak Electrolyte (W.E), Degree of ionization (α) of W.E increases.

# eg.:- CH_3COOH

$\alpha = \sqrt{\frac{K_a}{C}} = \sqrt{\frac{K_a}{n/V}} = \sqrt{\frac{K_a\times V_{sol^n}}{n}}$ $\alpha \propto \sqrt{\text{Vol. of sol}^n}$

$\boxed{\alpha^2 \propto V_{sol^n}}$

On Add^n of H_2O,
moles of WE Same
Conc (N or M) of WE decreases
$[H^+]$ decreases
α increases

# at Vol of sol^n (V_1) ⇒ α_1
" " " V_2 ⇒ α_2

$\boxed{\frac{\alpha_1^2}{\alpha_2^2} = \frac{V_1}{V_2}}$

Q. find % increase in ionization when sol^n of CH_3COOH ($K_a = 1.8\times10^{-5}$) is 100 times diluted?

Sol^n Initially vol of sol^n ⇒ V_1
final " " " ⇒ $100V_1 = V_2$

$\frac{\alpha_1^2}{\alpha_2^2} = \frac{V_1}{V_2} = \frac{1}{100}$

$\frac{\alpha_1}{\alpha_2} = \frac{1}{10}$

$\frac{\alpha_2 - \alpha_1}{\alpha_1}\times100 = \%$ increase

$\frac{10\alpha_1 - \alpha_1}{\alpha_1}\times100 = \%$ increase

$\boxed{900\% = \%\ \text{increase}}$

(iii) pH of Polyprotic Weak Acids (Having more than 1 H^+)

eg. H_2S, H_2CO_3, H_3PO_4 etc. → $K_{a_1} >> K_{a_2} >> K_{a_3}$

Q. find pH of 0.1M H_2S ($K_{a_1} = 10^{-7}$; $K_{a_2} = 10^{-14}$)
Also find $[S^{-2}]$ = ?

Sol^n

$H_2S_{(aq)} \rightleftharpoons H^+ + H\overset{-}{S}(aq)$
at eq^m: $(C - C\alpha_1)$, $C\alpha_1 + C\alpha_1\alpha_2 \approx C\alpha_1$, $C\alpha_1(1 - \alpha_2) \approx C\alpha_1$
$C(1-\alpha_1) \approx C$

$HS^-(aq) \rightleftharpoons H^+(aq) + S^{2-}(aq)$
at eq^m: $C\alpha_1(1-\alpha_2)$, $C\alpha_1\alpha_2 + C\alpha_1$, $C\alpha_1\alpha_2$
$C\alpha_1 - C\alpha_1\alpha_2$
$\approx C\alpha_1$

$C\alpha_1(1 + \alpha_2)$
$\approx C\alpha_1$

$\alpha_1 << 1$
$1 - \alpha_1 \approx 1$
$\alpha_2 << \alpha_1 << 1$
$1 - \alpha_2 \approx 1$
$1 + \alpha_2 \approx 1$

⇒

$H_2S \rightleftharpoons H^+ + HS^{(-)}$
at eq^m: C, $C\alpha_1$, $C\alpha_1$

$HS^- \rightleftharpoons H^+ + S^{2-}$
$C\alpha_1$, $C\alpha_1$, $C\alpha_1\alpha_2$

$K_{a_1} = \frac{[H^+][HS^-]}{[H_2S]} = \frac{(\cancel{C}\alpha_1)(C\alpha_1)}{\cancel{C}} = C\alpha_1^2$

$[H^+] = C\alpha_1$
$= C\sqrt{\frac{K_{a_1}}{C}} = \sqrt{C\cdot K_{a_1}}$
$pH = \frac{1}{2}[pK_{a_1} - \log C]$

$K_{a_2} = \frac{\cancel{[H^+]}[S^{2-}]}{\cancel{[HS^-]}}$ ⇒ $\boxed{K_{a_2} = [S^{2-}]}$

Conclusion
1) $[HS^-] = [H^+]$
2) $[H_2S]$ remains almost Same
3) H^+ is mainly due to first step
pH is calculated due to first step.

Solve Q→19 (Pg-95)

pH = 4.18
$-\log[H^+] = 4.18$
$\log[H^+] = -4.18$
$[H^+] = \text{antilog}[-4 - 0.18 + 1 - 1]$
$= \text{antilog}[-5 + 0.82]$
$= 6.73\times10^{-5}$

Note:- $\log y = 3.4$
$y = 10^{3.4}$ or antilog 3.4
$= \text{antilog}(3.4) = \text{antilog}(3 + 0.4)$
$= 2.5\times10^3$

# $\log 2 = 0.3$
$\log 3 = 0.47$
$\log 5 = 0.7$
$\log 7 = 0.84$
$\log 11 = 1.043$

$\log 2.5 = \log 5/2$
$= \log 5 - \log 2$
$= 0.7 - 0.3$
$= 0.4$

$\log 3.5 = \log 7 - \log 2$
$= 0.84 - 0.3$
$= 0.54$

$\log 6 = 0.77$

$\log 5.5 = \log\frac{11}{2} = \log 11 - \log 2$
$= 1.043 - 0.3$

Ⅲ S.A + W.A ⇒ $[H^+]$ is mainly due to Strong Acid

Q. 0.1M CH_3COOH + 0.2M HCl   α = ? pH = ? $[CH_3COO^-]$ = ?
$K_a(CH_3COOH) = 1.8\times10^{-5}$

Sol^n $CH_3COOH \rightleftharpoons H^+ + CH_3COO^-$
$C - C\alpha \approx C$, $C\alpha$, $C\alpha$
$H^+ + Cl^-$
0.2M, 0.2M

$K_a = \frac{[H^+]_{Total}[CH_3COO^-]}{[CH_3COOH]} = \frac{(C\alpha + 0.2)(C\alpha)}{C(1-\alpha)}$

$[H^+]_{Total} = C\alpha + 0.2$
$\approx 0.2M$

$\alpha << 1$
$1 - \alpha = 1$
$1 + \alpha = 1$

pH = $-\log(0.2)$
$= -\log(2\times10^{-1})$
$= 1 - \log 2$
$= 1 - 0.3$
$= 0.7$

$K_a = \frac{[H^+]_{S.A}(\cancel{C}\alpha)}{\cancel{C}}$

$1.8\times10^{-5} = 0.2\times\alpha$
$\boxed{\alpha = \frac{1.8\times10^{-5}}{0.2}}$

$[CH_3COO^-] = C\alpha$
$= 0.1\times\frac{1.8\times10^{-5}}{0.2}M$

Q→ 100ml, 0.1M HCN ($K_a = 10^{-6}$) + 100ml, 0.2M H_2SO_4
pH = ?

Sol^n:- $[HCN]_{new} = \frac{100\times0.1}{200}M = \frac{1}{20} = 0.05M$
$[H_2SO_4]_{new} = \frac{100\times0.2}{200}M = 0.1M$
$[H^+]_{Total} \approx [H^+]_{H_2SO_4} = 0.2M$
$pH = -\log(2\times10^{-1})$
$= \boxed{0.7}$

Ⅳ Complete Neutralization of Acid + Base

If same no. of equivalents (moles × n_f) of Acid & Base are mixed, then complete neutralisat^n takes place & in container Salt & H_2O are left.

Now ions of Salt will interact (React) with H_2O such that either $\bar{O}H$ or H^+ will be increased in H_2O to make sol^n Basic or Acidic respectively.

Cations ← Come from Base By removing $\overset{-}{O}H$
Anions ← " " Acid By " H^+

# ONLY those Cations & Anions will Hydrolyze (React with H_2O) which Come weak Electrolyte (WB, WA).

eg Salt $\boxed{CH_3COONa}$(aq)

$CH_3COO^- + \overset{H^+\bar{O}H}{H_2O(l)} \rightleftharpoons CH_3COOH + \boxed{\overset{-}{O}H}$ [Anionic Hydrolysis] $[OH^-] > [H^+]$ $\boxed{pH > 7}$ BASIC

$Na^+ + H_2O \longrightarrow$ ✗

Aq sol^n of CH_3COONa is Basic in Nature

Salt ⇒ NH_4Cl(aq) ⇐ NH_4OH + HCl

$NH_4^+ + H_2O \rightleftharpoons NH_4OH + H^+$ [(Cationic Hydrolysis) (CH)] $[H^+] > [OH^-]$ pH<7, Acidic

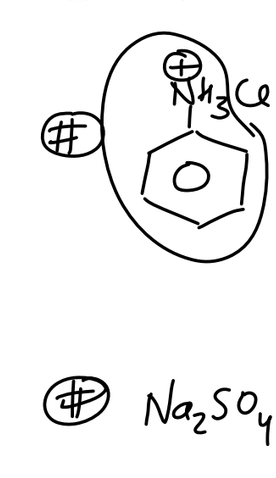
$Cl^- + H_2O \longrightarrow$ ✗

# KCl(aq) No Hydrolysis; pH = 7 → Neutral Salt

# KI(aq) " ; "

# NaCN(aq) → A.H ✓ $[OH^-] > [H^+]$ BASIC

#



C.H ✓
$[H^+] > [OH^-]$
Acidic Salt Sol^n
$\boxed{pH < 7}$

# Na_2SO_4(aq) ⇒ Neutral Salt

# NaCl(aq) ⇒ " "

# $NaHCO_3$ ⇒ A.H $\boxed{pH > 7}$